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(54) MANUFACTURE OF MARTENSITIC STAINLESS STEEL TUBE EXCELLENT IN TOUGHNESS AT LOW TEMPERATURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method of manufacturing a martensitic stainless steel tube having high strength of which the yield stress exceeds 650 MPa and also having excellent toughness at a low temperature.

SOLUTION: After martensitic stainless steel which has a composition consisting of, by weight, 0.10-0.18% C, ≤0.5% Si, 0.1-1.5% Mn, ≤0.02% P, ≤0.01% S, 12-14% Cr, 1-3% Ni, ≤0.3% Al, 0.001-0.08% N and the balance Fe with inevitable impurities and further, containing, if necessary, one or ≥2 kinds among ≤0.5% Mo, ≤1.5% Cu, 0.001-0.05% Ti and 0.001-0.01% Ca, is formed into a tube by hot rolling, if necessary, heated up to a temperature region between an Ac₃ point and 950°C and successively cooled down to a room temperature at a velocity not lower than an air cooling velocity, heated up to a temperature between the Ac₁ point and the Ac₃ point, successively cooled down to the room temperature and then, tempering-treated at a temp. not higher than the Ac₁ point.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the martensitic stainless steel excellent in low-temperature toughness.

[0002]

[Description of the Prior Art]Martensitic stainless steel was excellent in intensity and CO-proof₂ corrosiveness, and since it is comparatively cheap, it has been applied as an oil well pipe around 1980, so that it may be represented by AISI420 steel. Usually, after tube manufacturing, although quenching and tempering treatment are carried out and it is manufactured, since low-temperature toughness is insufficient, use in a cold district is restricted. . As [see / then, / JP,H3-75308,A etc. / as a manufacturing method for acquiring the outstanding low-temperature toughness] The manufacturing method which enlarges the cooling rate after austenitizing and controls a deposit of big and rough chromium carbide, The manufacturing method which enlarges the cooling rate after annealing which is looked at by JP,H5-263134,A etc., and controls a deposit of big and rough chromium carbide, The manufacturing method which enlarges the heating rate at the time of austenitizing which is looked at by JP,H4-210453,A etc., and shortens retention time, and prevents big and rough-ization of austenite particle diameter, The manufacturing method etc. which use a thermomechanical treatment method so that JP,S63-238217,A, JP,S63-241117,A, etc. may see are proposed. However, the actual condition is that sufficient low-temperature toughness is not acquired in the high strength material with which yield stress exceeds 650Mpa very in addition in these plans.

[0003]

[Problem(s) to be Solved by the Invention]This invention tends to solve a problem which was described above. The purpose is to provide the manufacturing method of the martensitic stainless steel which has the low-temperature toughness which has the high intensity in which yield stress exceeds 650Mpa, and was excellent.

[0004]

[Means for Solving the Problem]This invention persons perform various heat treatments to various raw materials in which ingredients differ, As a result of repeating research about low-temperature toughness, after forming Cr steel by the hot-rolling method 13% which adjusted C 0.18% or less 0.10% or more, and adjusted nickel to 3% or less 1% or more, Ac1 -- beyond point Ac3 -- retained austenite serving as an organization which

distributed minutely, and in a martensite host phase, if temperature below a point is heated and followed and it cools to a room temperature, It is this Ac1 The knowledge of the ability to prevent [that low-temperature toughness will improve substantially if tempering treatment is carried out at temperature below a point, and] a deposit of a delta ferrite which will degrade hot-working nature if it is in the above-mentioned component range was carried out.

[0005]A place which constitutes this invention based on such knowledge, and is made into the gist, At weight %, it is C. : 0.10 to 0.18%, less than Si:0.5%, Mn : [0.1 to 1.5% or less,] P : 0.02% or less, S : 0.01% or less, Cr : [12 to 14%,] nickel: 1 to 3%, less than aluminum:0.3%, N : 0.001 to 0.08% is contained, If needed Less than Mo:0.5% and less than Cu:1.5%. Ti: 0.001-0.05%, Ca : After it contains 0.001 to 0.01% of one sort, or two sorts or more and the remainder forms martensitic stainless steel which consists of Fe and inevitable impurities by the hot-rolling method, Necessity is accepted and it is Ac3.

Beyond a point heats and follows a temperature region 950 ** or less, and it cools speed more than air cooling to a room temperature, Ac1 -- beyond point Ac3 -- heating and following temperature below a point and cooling to a room temperature -- after an appropriate time and Ac1 -- it is a manufacturing method of a martensitic stainless steel tube excellent in low-temperature toughness carrying out tempering treatment at temperature below a point.

[0006]

[Embodiment of the Invention]Hereafter, this invention is explained in detail. It is AISI420 steel (0.2%C-13%Cr) which is a typical steel type of martensitic stainless steel Ac1 If beyond a point heats to the temperature of three or less Ac(s), reverse transformation austenite will generate, but. Then, since the austenite which carried out the reverse transformation will metamorphose into martensite if it cools to a room temperature, retained austenite is hardly generated. However, it is steel of the ingredient which reduced the amount of C to 0.18% or less, and added nickel which is an austenite stabilization element 1% or more Ac1 Beyond point Ac3 Since nickel will condense in the austenite phase which carried out the reverse transformation and the stability of austenite will become high, if it heats to the temperature below a point, Austenite is held even if it cools to a room temperature. That is, retained austenite serves as an organization which distributed minutely into a martensite host phase. It is this Ac1 If tempering treatment is carried out at the temperature below a point, low-temperature toughness will improve substantially. It is **Ac1 when too large, although it is so good that raising the stability of the austenite which carried out the reverse transformation has many amounts of nickel. Since the point fell and the range which can be intensity refined was restricted, the maximum of nickel addition was made into 3%. Ac1 -- beyond point Ac3 -- the minimum was made into 0.1% in order to prevent the generation of the delta ferrite which degrades hot-working nature although it is moderate whose amount of C is low in order to prevent carrying out a martensitic transformation, when cooling the martensite which heated and carried out the reverse transformation to the temperature below a point to a room temperature.

[0007]Ac1 after forming a tube by the hot-rolling method -- beyond point Ac3 -- before performing heat treatment which heats and follows the temperature below a point and is cooled to a room temperature -- Ac3 -- if heat treatment as for which beyond a point heats and follows a temperature region 950 ** or less and which is cooled the speed more

than air cooling to a room temperature is performed, low-temperature toughness can be raised further. If this heats and follows the coexisting temperature range of austenite and undissolved carbide and is cooled the speed more than air cooling to a room temperature after it forms a tube by the hot-rolling method, It is because a deposit of the big and rough chromium carbide to the grain community which can carry out grain refining of the austenite particle diameter according to the depressor effect of the austenite grain growth by grain boundary pinning of undissolved carbide, and is cooled the speed more than air cooling since there is little dissolution carbon can be controlled.

[0008]Necessity is accepted and it is Ac3. Beyond a point heats and follows a temperature region 950 ** or less, and it cools the speed more than air cooling to a room temperature, Ac1 -- beyond point Ac3 -- the 2-phase composite structure of the martensite which heated and followed the temperature below a point and was cooled the speed more than air cooling to the room temperature, and retained austenite -- Ac1 -- necessary intensity and toughness being acquired if tempering treatment is carried out at the temperature below a point, but. Tempering temperature is Ac1. Since yield stress will decline rapidly if a point is exceeded, intensity cannot be built stably. So, it is tempering temperature Ac1 Below the point carried out.

[0009]The Reason for ingredient limitation of the martensitic stainless steel tube in this invention is as follows.

C: Since degradation of corrosion resistance and toughness arose when it exceeded 0.18%, C made the maximum 0.18%. Since a delta ferrite deposits in a hot-working temperature region and hot-working nature was degraded when less than 0.10%, the degree was made into 0.10%.

[0010]Si:Si is set like a steelworker and added as a deoxidizer. Since toughness deteriorated when contained exceeding 0.5%, the maximum was made into 0.5%.

[0011]Although Mn:Mn is an austenite stabilization element and is effective in rolling crack prevention by controlling the deposit of a delta ferrite at the time of hot working, Since the effect was not revealed at less than 0.1%, but the grain community intensity added exceeding 1.5% was reduced and toughness deteriorated, the optimal addition range was made into 0.1% - 1.5%.

[0012]P: Although P was an impurity element which carries out a segregation to a grain boundary, reduces grain boundary intensity to it, and degrades toughness and its as much as possible low was desirable, the maximum was made into 0.02% in consideration of the level which can be reached and cost of actual condition refinement art.

[0013]S: Although S was an impurity element which degrades hot-working nature and toughness and its as much as possible low was desirable, the maximum was made into 0.01% in consideration of the level which can be reached and cost of actual condition refinement art.

[0014]Although Cr:Cr was a basic element of corrosion-resistant improvement and needed not less than 12% of addition to acquire sufficient corrosion resistance, it was also a ferrite stabilization element, and since a delta ferrite would deposit at the time of hot working and hot-working nature would be deteriorated if too large, the maximum was made into 14%.

[0015]It is an austenite stabilization element, nickel:nickel is effective in carrying out fine dispersion of the retained austenite into a martensite host phase, and raising toughness while it deters generation of the delta ferrite which leads to a rolling crack, but.

It is Ac1, when the effect is not revealed at less than 1% but it adds exceeding 3%. Since the point fell and the range which can be intensity refined was restricted, the optimal addition was made into 1% - 3%.

[0016]aluminum:aluminum is added in order to set like a steelworker and to promote deoxidation and desulfurization. Since toughness deteriorated when contained exceeding 0.3%, the maximum was made into 0.3%.

[0017]N: although N had an effect which forms a nitride and controls coarsening, at less than 0.001%, it was not revealed, and since toughness would deteriorate if it adds exceeding 0.08%, the effect made the optimal addition 0.001% - 0.08%.

[0018]Although Mo:Mo controls the grain boundary segregation of P, and is an element effective in the improvement in toughness and it added if needed, it was also a ferrite stabilization element, and since a delta ferrite would deposit at the time of hot working and hot-working nature would be deteriorated if too large, the maximum was made into 0.5%.

[0019]Are an austenite stabilization element, Cu:Cu deters generation of a delta ferrite, since it is effective in rolling crack prevention, it adds it if needed, while it is an element effective in the improvement in corrosion resistance like nickel, but. Since hot-working nature deteriorated remarkably in order to carry out a segregation to the grain community added exceeding 1.5% superfluously and to reduce grain boundary intensity on it, the maximum was made into 1.5%.

[0020]Although Ti:Ti controls hot-working nature degradation by S and it adds if needed, at less than 0.001%, even if the effect was not revealed but it added exceeding 0.05%, the effect was saturated, and in order to deposit a conversely big and rough nitride and to reduce toughness, it made the optimal addition 0.001% - 0.05%.

[0021]Although Ca:Ca controls hot-working nature degradation by S and it adds if needed, Since Ca system inclusion increased and sulfide-proof stress crack nature deteriorated when the effect was not revealed at less than 0.001% but it added exceeding 0.01%, the optimal addition was made into 0.001% - 0.01%.

[0022]This invention steel is mainly formed by joint ductlessness by the method of hot-rolling the Mannesmann method. With the method of rolling the Mannesmann method here, the tubing material of a rectangular cross section or a round section is used, After punching by the press sirloin terebration or the Mannesmann terebration, it extends with a skew rolling machine (design elongator) if needed, and the process of forming the tube by the plug mill or the mandrel mill further is meant.

[0023]

[Example]It refined to the high intensity which heat-treats on the conditions shown in Table 1 to the outer diameter of 177.8 mm of the ingredient shown in Table 1, and the steel pipe of a with a thickness of 11.5 mm hot-rolling as, and exceeds 650Mpa, the V-notched charpy impact test (JIS Z 2242, a full size, the direction of L) was done, and it asked for fracture transition temperature. It asked for yield stress by the tensile test (JIS Z 2241). A result is shown in Table 1. In Table 1, two-phase region processing is Ac1. Beyond point Ac3 Heat treatment which heats and follows the temperature below a point and is cooled to a room temperature is meant.

[0024]According to this invention (No.1-No.10), it is clear that yield stress has the high intensity exceeding 650Mpa, and the good low-temperature toughness not more than -30 ** is acquired for fracture transition temperature. In particular, it is Ac1. Beyond point

Ac3 If heat treatment which heats and follows the temperature region not more than beyond Ac3 point 950 **, and is cooled the speed more than air cooling to a room temperature is performed before performing heat treatment heated to the two-phase region temperature below a point, it is clear that the further outstanding low-temperature toughness is acquired (this invention No.9, 10). On the other hand, in a comparative example (No.11-No.18), fracture transition temperature is all 0 ** or more, and good low-temperature toughness is not acquired.

[0025]

[Table 1]

序号	化学成分(wt-%)										24時間耐候性 温度上昇 温度下降							照射時間 温度(℃)		EVA 吸光度 (A _{430nm})			
	C	Si	Al	P	S	Cr	N	Mo	Ca	Ti	Fe	Co	Ni	Cr (Cr ₂₃)	Mo (Mo ₂₃)	Fe (Fe ₂₃)	Co (Co ₂₃)	Ni (Ni ₂₃)					
1	0.6	0.3	0.1	0.018	0.007	13.2	0.01	0.02	-1.9	-	-	-	-	-	-	-	-	-	-	-	-	-	
2	0.6	0.2	0.1	0.017	0.005	12.9	0.02	0.03	-1.3	-	-	-	-	-	-	-	-	-	-	-	-	-	
3	0.45	0.4	0.4	0.012	0.004	13.1	0.01	0.01	-1.7	-	-	-	-	-	-	-	-	-	-	-	-	-	
4	0.18	0.3	0.7	0.009	0.006	12.8	0.03	0.02	-1.1	3.2	-	-	-	-	-	-	-	-	-	-	-	-	
5	0.18	0.3	0.5	0.016	0.005	13.1	0.02	0.02	-1.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-	
6	0.18	0.1	0.6	0.016	0.005	13.1	0.02	0.02	-1.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-	
7	0.18	0.1	0.6	0.016	0.005	13.1	0.02	0.02	-1.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-	
8	0.15	0.4	0.9	0.013	0.004	12.9	0.01	0.01	-2.1	-	-	0.93	0.030	-	-	-	-	-	-	-	-	-	-
9	0.15	0.4	0.4	0.017	0.003	2.5	0.01	0.03	2.7	-	-	-	0.93	0.030	-	-	-	-	-	-	-	-	-
10	0.17	0.2	0.3	0.017	0.006	12.2	0.17	0.07	1.3	-	-	-	-	-	22.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	
11	0.20	0.3	0.3	0.020	0.007	3.2	0.08	0.01	0.1	-	-	-	94.0	48.0	-	-	-	-	-	-	-	-	-
12	0.22	0.3	0.7	0.020	0.006	12.7	0.01	0.02	0.1	-	-	-	90.0	79.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	
13	0.19	0.3	0.4	0.016	0.008	11.7	0.01	0.01	0.2	-	-	-	90.0	82.0	-	-	-	-	-	-	-	-	-
14	0.22	0.3	0.6	0.016	0.006	12.9	0.02	0.02	0.3	-	8.4	-	-	-	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	
15	0.22	0.3	0.6	0.016	0.006	12.9	0.02	0.02	0.3	-	-	-	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	
16	0.22	0.3	0.6	0.021	0.006	13.1	0.03	0.02	0.4	-	-	-	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	81.5	
17	0.21	0.1	0.2	0.025	0.005	2.7	0.17	0.01	0.1	-	-	-	-	-	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	
18	0.22	0.1	0.2	0.027	0.002	2.6	0.02	0.01	0.2	-	-	-	-	-	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	

[0026]

[Effect of the Invention] According to this invention, the manufacturing method of the

martensitic stainless steel tube which has the low-temperature toughness which has the high intensity in which yield stress exceeds 650Mpa, and was excellent is provided as mentioned above.

[Translation done.]